



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>B01J 23/50, 37/06, C07D 301/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/15335</b> <b>(43) International Publication Date:</b> 23 March 2000 (23.03.00)
<b>(21) International Application Number:</b> PCT/EP99/06725 <b>(22) International Filing Date:</b> 10 September 1999 (10.09.99) <b>(30) Priority Data:</b> 60/100,196 14 September 1998 (14.09.98) US <b>(71) Applicant:</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). <b>(72) Inventor:</b> LOCKEMEYER, John, Robert; 3403 Stoney Mist Drive, Sugar Land, TX 77479 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> EPOXIDATION CATALYST CARRIER, PREPARATION AND USE THEREOF <b>(57) Abstract</b> <p>There is provided a catalyst carrier comprising a refractory inorganic material having a sodium solubilization rate no greater than 5 ppmw/5 minutes. There is further a catalyst comprising a refractory inorganic material carrier having a sodium solubilization rate no greater than 5 ppmw/5 minutes; and one or more catalytically reactive metals deposited on said carrier. There is also provided a catalyst suitable for the vapour phase production of alkylene oxide from olefins and oxygen comprising an alumina-based carrier having a sodium solubilization rate no greater than 5 ppmw/ 5 minutes; and catalytically reactive silver deposited on said carrier.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CN	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## EPOXIDATION CATALYST CARRIER, PREPARATION AND USE THEREOF

Field of the Invention

The invention relates to a catalyst with improved catalytic properties, particularly a catalyst suitable for the preparation of epoxides.

5 Background of the Invention

Methods have been described for lowering the total concentration of soluble species in the bulk of a catalyst carrier. These methods generally involve a process by which the carrier is manufactured in such a way so as to lower the concentration of those species throughout the bulk of the carrier. These approaches limit the formulation of carriers, often times with undesirable consequences such as high carrier density.

15 US Patent No. 4,797,270 discloses water washing to reduce the sodium content of an alumina powder. The pH of the wash water may need to be adjusted for extraction of other metals and Japanese patent JP56164013 discloses the use of a low pH (acid) to extract uranium and thorium from a calcined  $\alpha$ -alumina raw material.

20 US Patent Nos. 4,361,504 and 4,366,092 suggest that ethylene oxide catalyst be water washed after the deposition of silver or silver/gold on the carrier. EP-211521 discloses washing of a catalyst with hot water to remove basic materials left on the catalyst from a silver impregnation process or the physical deposition of alkali metals. US Patent No. 4,367,167 discloses a process for a supported catalyst wherein an impregnated support is immersed in an inert water immiscible organic solvent containing a dissolved aliphatic amine. US Patent  
25  
30 No. 4,810,689 discloses depositing a silver compound, decomposing the silver compound to silver in the presence

- 2 -

of an alkali metal compound, removing organic deposits by washing and introducing fresh alkali metal by impregnation during or after the washing stage. U.S. Patent Nos. 4,186,106 and 4,125,480 disclose washing with an inert liquid after deposition of the catalytic metal and before deposition of a promoter material.

The prior art remains concerned with the total amount of impurities; i.e., impurities throughout the bulk. Unfortunately, the impurity removal techniques taught typically attack the carrier itself. It has now been found that controlling the solubilization rate of certain species, and in particular sodium, on a carrier surface results in a catalyst with improved catalytic properties.

#### Summary of the Invention

According to the present invention, there is provided a catalyst carrier having a sodium solubilization rate, as measured by the amount released by immersion in 3:1 w/w of boiling water, of no greater than 5 ppmw, basis the total weight of the carrier, per 5 minutes.

A further embodiment of the invention provides a process for preparing said catalyst carrier wherein said sodium solubilization rate is achieved by a means effective in rendering ionizable species present on the surface of the carrier ionic and removing at least part of that species, or rendering the ionizable species insoluble, or rendering the ionizable species immobile.

Another embodiment of the invention provides a catalyst, especially a catalyst suitable for the vapour phase epoxidation of olefins, the catalyst comprising said carrier and one or more catalytically reactive metals and optionally one or more promoting materials deposited thereon.

#### Detailed Description of the invention

It has been found that carriers which have a controlled solubilization rate, in particular controlled

- 3 -

sodium and/or soluble silicate solubilization rates, provide catalysts with improved catalytic properties, such as activity, selectivity and activity and/or selectivity performance over time. Controlling the solubilization rate is believed to work to improve the properties of most catalysts, no matter how impure the bulk carrier material. Further, controlling the solubilization rate will work for organic or inorganic carriers.

The typical carrier of the invention has a sodium solubilization rate in boiling water which is controlled to be no greater than 5 ppmw/5 minutes. "Solubilization rate" as used herein refers to the measurable solubilization rate of the sodium in a solvent after the carrier is placed in the solvent for a specified time and at a ratio of boiling solvent to carrier of 3:1. Thus, a solubilization rate in boiling water of 5 ppmw sodium/5 minutes is the amount of sodium measured in the water after the carrier has been in the boiling water for five minutes.

Carriers are commonly inorganic materials such as, for example, alumina-, silica-, or titania-based compounds, or combinations thereof, such as alumina-silica carriers. Carriers may also be made from carbon-based materials such as, for example, charcoal, activated carbon, or fullerenes.

Ionizable species typically present on the inorganic type carriers include sodium, potassium, aluminates, soluble silicate, calcium, magnesium, aluminosilicate, and combinations thereof. Of particular concern are the ionizable anionic species present on the surface, particularly ionizable silicates. The solubilization rate of silicates may be measured by inductively coupled plasma (ICP) techniques and the amount of silicon species on a surface may be measured by x-ray photoelectron

- 4 -

spectroscopy (XPS). However, since sodium is soluble in the same solutions that silicates are soluble in, the solubilization rate of sodium becomes a simpler check of the ionic species removal and it has been chosen as the indicator to define the present invention. Another measurement technique is to measure the electrical conductivity of the treatment solution.

As used herein, the "surface" of the carrier is that area of the carrier which may be measured by the standard method of Brunauer, Emmett and Teller (B.E.T). Specifically, the surface of the carrier is the site at which reaction takes place. Lowering the concentration of ionizable species on the surface of the carrier has been found to be an effective and cost efficient means of achieving the desired surface sodium solubilization rate. An "ionizable" species is a species which is capable of being rendered ionic, whereas the term "ionic" or "ion" refers to an electrically charged chemical moiety.

Lowering the surface solubilization rate of ionizable species may be accomplished by any means which is effective in (i) rendering the ionizable species ionic and removing the species, or (ii) rendering the ionizable species insoluble, or (iii) rendering the ionizable species immobile. However, use of aggressive media is discouraged as these media tend to dissolve the carrier, extract too much material from the bulk, and generate acidic or basic sites in the pores. Acids, which are considered aggressive media, will remove the cations on a carrier but are fairly ineffectual in removing the undesirable anions, such as silicates. Effective means of lowering concentration include washing the carrier; ion exchange; volatilizing, precipitating, or sequestering the impurities; causing a reaction to make the ionizable species on the surface insoluble; and combinations thereof. The bulk carrier may be treated, or the raw

- 5 -

materials used to form the carrier may be treated before the carrier is manufactured. Even greater improvements in solubilization rate control are seen when both the carrier raw materials and the finished carrier are treated.

To make a catalyst from the carrier, the carrier is typically impregnated with metal compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to deposit or impregnate a catalytically effective amount of metal on the carrier. As used herein, "catalytically effective amount" means an amount of metal that provides a measurable catalytic effect. For example, a catalytically effective amount of metal when referring to an olefin epoxidation catalyst is that amount of metal which provides a measurable conversion of olefin and oxygen to alkylene oxide. In addition, one or more promoters may also be deposited on the carrier either prior to, coincidentally with, or subsequent to the deposition of the catalytically reactive metal. The term "promoter" as used herein refers to a component which works effectively to provide an improvement in one or more of the catalytic properties of the catalyst when compared to a catalyst not containing such component.

Further improvement in the catalyst properties are seen when the metal deposition is effected by contacting the carrier with an impregnation solution whose hydrogen ion activity has been lowered. "Hydrogen ion activity" as used herein is the hydrogen ion activity as measured by the potential of a hydrogen ion selective electrode. As used herein, a solution with "lowered" hydrogen ion activity refers to a solution whose hydrogen activity has been altered by the addition of a base, such that the hydrogen ion activity of the altered solution is lowered compared to the hydrogen ion activity of the same solution in an unaltered state. The base selected to

- 6 -

alter the solution may be chosen from any base or compound with a  $pK_b$  lower than the original impregnation solution. It is particularly desirable to choose a base which does not alter the formulation of the impregnation solution; i.e., which does not alter the desired metals concentration in the impregnation solution and deposited on the carrier. Organic bases will not alter the impregnation solution metals concentrations, examples of which are tetraalkylammonium hydroxides and 1,8-bis-(dimethylamino)-naphthalene. If changing the metals concentration of the impregnation solution is not a concern, metal hydroxides may be used.

When the impregnation solution is at least partially aqueous, an indication of the change in the hydrogen activity may be measured with a pH meter, with the understanding that the measurement obtained is not pH by a true, aqueous definition. "Measured pH" as used herein shall mean such a non-aqueous system pH measurement using a standard pH probe. Even small changes in the "measured pH" from the initial impregnation solution to that with added base are effective and improvements in catalytic properties continue as the "measured pH" change increases with base addition. High base additions do not seem to adversely affect catalyst performance; however, high additions of hydroxides have been seen to cause sludging of the impregnation solution, creating manufacturing difficulties. When the base addition is too low, the hydrogen ion activity will not be affected. The hydrogen ion activity lowering procedure is also quite effective when used by itself; i.e., when no ionizable species concentrations are lowered prior to impregnation.

The impregnated carrier, also known as a catalyst precursor, is dried in the presence of an atmosphere which also reduces the catalytic metal. Drying methods



- 7 -

known in the art include steam drying, drying in an atmosphere with a controlled oxygen concentration, drying in a reducing atmosphere, air drying, and staged drying using a suitable ramped or staged temperature curve.

5           By way of example, the invention will be described in more detail for a catalyst suitable for the vapour phase production of epoxides, also known as an epoxidation catalyst.

10           An epoxidation catalyst typically comprises an inorganic carrier, for example an alumina-based carrier such as  $\alpha$ -alumina, with one or more catalytically reactive metals deposited on the carrier. The carrier typically contains certain ionizable species, for example an  $\alpha$ -alumina carrier, typically contains species  
15 including sodium, potassium, aluminates, soluble silicates, calcium, magnesium, aluminosilicates, and combinations thereof. It has been found that silicates, and certain other anions, are particularly undesirable ionizable species in an epoxidation catalyst.

20           According to the invention, the sodium solubilization rate in 3:1 w/w of boiling water is controlled to less than 5 ppmw Na/5 minutes. The solubilization rate may be controlled by lowering the concentration of ionizable species on the surface, as described above.

25           The carrier having the controlled solubilization rate is impregnated with metal ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause the desired deposition on the carrier. When silver is the deposition material, a  
30 typical deposition is from 1 to 40 wt%, preferably from 1 to 30 wt% of silver, basis the weight of the total catalyst. The impregnated carrier is subsequently separated from the solution and the deposited metal(s) compound is reduced to metallic silver.

- 8 -

One or more promoters may be deposited either prior to, coincidentally with, or subsequent to the deposition of the metal. Promoters for epoxidation catalysts are typically selected from sulphur, phosphorus, boron, fluorine, Group IA through Group VIII metals, rare earth metals, and combinations thereof. The promoter material is typically compound(s) and/or salt(s) of the promoter dissolved in a suitable solvent.

For olefin epoxidation oxide catalysts, Group IA metals are typically selected from potassium, rubidium, cesium, lithium, sodium, and combinations thereof; with potassium and/or cesium and/or rubidium being preferred. Even more preferred is a combination of cesium plus at least one additional Group IA metal, such as cesium plus potassium, cesium plus rubidium, or cesium plus lithium. Group IIA metals are typically selected from magnesium, calcium, strontium, barium, and combinations thereof, Group VIII transition metals are typically selected from cobalt, iron, nickel, ruthenium, rhodium, palladium, and combinations thereof; and rare earth metals are typically selected from lanthanum, cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof. Non-limiting examples of other promoters include pererrhenate, sulphate, molybdate, tungstate, chromate, phosphate, borate, sulphate anion, fluoride anion, oxyanions of Group IIIB to VIB, oxyanions of an element selected from Groups III through VIIB, alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups IIIA to VIIA and IIIB through VIIB. The amount of Group IA metal promoter is typically in the range of from 10 ppm to 1500 ppm, expressed as the metal, by weight of the total catalyst, and the Group VIIB metal is less than 3600 ppm, expressed as the metal, by weight of the total catalyst.

- 9 -

For further improvement in catalytic properties, the hydrogen ion activity of the impregnation solution is lowered, such as by the addition of a base. The typical impregnation solution for an epoxidation catalyst begins quite basic, so a strong base is used to further lower the hydrogen ion activity. Examples of strong bases include alkyl ammonium hydroxide such as tetraethylammonium hydroxide, lithium hydroxide and cesium hydroxide. In order to maintain the desired impregnation solution formulation and metal loading, an organic base such as tetraethylammonium hydroxide is preferred. Base additions in these systems typically result in a "measured pH" change ranging up to about 3, realizing that the "measured pH" is not a true pH since the impregnation system is not aqueous.

The carrier employed in these catalysts in its broadest aspects can be any of the large number of conventional, porous refractory catalyst carriers or carrier materials which are considered relatively inert. Such conventional materials are known to those skilled in the art and may be of natural or synthetic origin. Carriers for epoxidation catalysts are preferably of a macroporous structure and have a surface area below about  $10 \text{ m}^2/\text{g}$  and preferably below about  $3 \text{ m}^2/\text{g}$ . Examples of carriers for different catalysts are the aluminium oxides (including the materials sold under the trade name "Alundum"), charcoal, pumice, magnesia, zirconia, kieselguhr, fuller's earth, silicon carbide, porous agglomerates comprising silica and/or silicon carbide, silica, magnesia, selected clays, artificial and natural zeolites, alkaline earth carbonates, and ceramics. Refractory carriers especially useful in the preparation of olefin epoxidation catalysts comprise the aluminous materials, in particular those comprising  $\alpha$ -alumina. In the case of  $\alpha$ -alumina-containing carriers, preference is

- 10 -

given to those having a specific surface area as measured by the B.E.T. method of from 0.03 to 10 m<sup>2</sup>/g, preferably from 0.05 to 5 m<sup>2</sup>/g, more preferably from 0.1 to 3 m<sup>2</sup>/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmett, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

Certain types of  $\alpha$ -alumina containing carriers are particularly preferred. These  $\alpha$ -alumina carriers have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from 0.1 to 3 m<sup>2</sup>/g, preferably from 0.1 to 2 m<sup>2</sup>/g, and water pore volumes of from 0.10 to about 0.55 ml/g. Manufacturers of such carriers include Norton Chemical Process Products Corporation and United Catalysts, Inc. (UCI).

The resulting epoxidation catalysts just described are used for the vapour phase production of epoxides, especially ethylene oxide. A typical epoxidation process involves loading catalysts into a reactor. The feedstock to be converted, typically a mixture of ethylene, oxygen, carbon dioxide, nitrogen and ethyl chloride, is passed over the catalyst bed at elevated pressure and temperature. The catalyst converts the feedstock to an outlet stream product which contains ethylene oxide. Nitrogen oxides (NO<sub>x</sub>) may also be added to the feedstock to boost catalyst conversion performance.

The following Examples will illustrate the invention.

- 11 -

ExamplesCarriers

Table I shows the carriers used for the Examples.

TABLE I

Carrier	A	B	C	D
B.E.T. Surface Area (m <sup>2</sup> /g) (a)	0.84	0.97	0.78	0.87
Water Absorption (%)	39.7	46.2	37.6	43.4
Crush Strength (kg) (b)	6.53	8.07	12.29	5.44
Total Pore Volume (ml/g) (c)	0.408	0.460	0.390	
Median Pore Diameter (microns) (c)	1.8	2.7	1.3	
SiO <sub>2</sub> (%w)	0.5	0.8	0.1	0.5
Bulk Acid-Leachable Na (ppmw)	438	752	186	339
Bulk Acid-Leachable K (ppmw)	85	438	109	37
Bulk Acid-Leachable Ca (ppmw)	207	508	526	123
Bulk Acid-Leachable Al (ppmw)	744	1553	657	499
Bulk Acid-Leachable SiO <sub>2</sub> (ppmw)	808	1879	1560	600
alpha-Alumina (% w)	Bal.	Bal.	Bal.	Bal.

a Method of Brunauer, Emmett and Teller, loc. cit.

b Flat Plate Crush Strength, single pellet.

c Determined by mercury intrusion to  $3.8 \times 10^8$  Pa using Micromeritics Autopore 9200 or 9210 (130° contact angle, 0.473 N/m surface tension of Hg).

#### Carrier Water Washing Procedures for Examples 1, 2, 3, 4, 5, 6, 7, 12

Carrier washing was carried out by immersing 100 grams of carrier in 300 grams of boiling de-ionized water for 15 minutes. The carrier was then removed and placed in a fresh 300 grams of boiling water for another 15 minutes. This procedure was repeated once more for a total of three immersions, at which point the carrier was

- 12 -

separated from the water and dried in a well ventilated oven at 150 °C for 18 hours. The dried carrier was then used for preparation of a catalyst by the procedures outlined in the following Examples.

5     Impregnation Solution

A silver-amine-oxalate stock solution was prepared by the following procedure:

10     415 g of reagent-grade sodium hydroxide were dissolved in 2340 ml de-ionized water and the temperature was adjusted to 50 °C.

1699 g high purity "Spectropure" silver nitrate were dissolved in 2100 ml de-ionized water and the temperature was adjusted to 50 °C.

15     The sodium hydroxide solution was added slowly to the silver nitrate solution, with stirring, while maintaining a solution temperature of 50 °C. The mixture was stirred for 15 minutes, then the temperature was lowered to 40 °C.

20     Water was removed from the precipitate created in the mixing step and the conductivity of the water, which contained sodium and nitrate ions, was measured. An amount of fresh deionized water equal to the amount removed was added back to the silver solution. The solution was stirred for 15 minutes at 40 °C. The process  
25     was repeated until the conductivity of the water removed was less than 90 µmho/cm. 1500 ml fresh deionized water was then added.

30     630 g of high-purity oxalic acid dihydrate were added in approximately 100 g increments. The temperature was kept at 40 °C and the pH was kept above 7.8.

Water was removed from the mixture to leave a highly concentrated silver-containing slurry. The silver oxalate slurry was cooled to 30 °C.

35     699 g of 92 %w ethylenediamine (8% de-ionized water) was added while maintaining a temperature no greater than

- 13 -

30 °C. The resulting solution contained approximately 27-33 %w silver.

Enough 45 %w aqueous CsOH and water was added to this solution to give a finished catalyst having 14.5 %w silver and a desired cesium loading (see Examples).

#### Sodium Measurement Procedures

The sodium solubilization rate of selected carriers was determined by measuring the sodium content of the extracting medium with an Orion model no. 8611BN sodium selective electrode connected to an Orion model 290A voltmeter. In a typical experiment, 300 grams of carrier was boiled in 900 grams of de-ionized water for a total of fifteen minutes. During this period, 3 ml aliquots were taken at predetermined intervals. The sodium content of each aliquot was analyzed at 25 °C using procedures well established for ion selective electrodes. The sodium concentration in the solution sampled at 5 minutes is used to evaluate the carrier as being a good or poor candidate for catalyst preparation. Results are given in Table II.

TABLE II. Sodium Solubilization Rates per 5 minutes for Selected  $\alpha$ -Alumina Carriers

Carrier	Bulk Na Unwashed Carrier (ppmw) <sup>a</sup>	Extracted Na Unwashed Carrier (ppmw)	Extracted Na Washed Carrier (ppmw)
A	438	9.2	1.3
A <sup>b</sup>	438	9.2	1.2
B	752	9.2	1.8
C	186	10.2	-

<sup>a</sup> From Table I.

<sup>b</sup> Following ammonium acetate exchange as described in Example 8.

- 14 -

pH Measurement Procedures

Silver solution pH measurements were done using a Metrohm model 744 pH meter, employing a model 6.0220.100 combination electrode and a Pt 100 model 6.1110.100 resistance thermometer for temperature compensation. The meter was calibrated with commercially available buffer solutions before each use. In a typical measurement, a 50 ml aliquot of the doped silver solution to be used for a catalyst impregnation was filtered into a 100 ml glass beaker through a 2 micron filter attached in-line to a plastic syringe. The pH probe was lowered into the magnetically stirred solution, and the reading obtained after 3 minutes was recorded as the equilibrated pH. The probe was cleaned between each measurement with deionized water, and checked for calibration. Special care was taken to prevent accumulation of AgCl solids on the electrode membrane. Such accumulation was removed by soaking the probe in ammonium hydroxide solution, as recommended by the manufacturer.

Example 1

A catalyst precursor was prepared from Carrier A by first subjecting the carrier to carrier washing. Following the wash, approximately 30 grams of washed Carrier A were placed under a 3.33 kPa vacuum for 1 minute at ambient temperature. Approximately 50 grams of the impregnating solution was then introduced to submerge the carrier, and the vacuum was maintained at 3.33 kPa for an additional 3 minutes. The cesium target was 450 ppm/gram finished catalyst. The vacuum was then released and the excess impregnating solution was removed from the catalyst pre-cursor by centrifugation at 500 rpm for two minutes. The catalyst pre-cursor was then dried while being shaken at 240 °C for 4 minutes in a stream of air flowing at 11.3 m<sup>3</sup>/hr.



- 15 -

Example 1a (Comparative)

Carrier A was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 2

Carrier B was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst.

Example 2a (Comparative)

Carrier B was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 3

Carrier C was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 300 ppm/gram finished catalyst.

Example 3a (Comparative)

Carrier C was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 360 ppm/gram finished catalyst.

Example 4

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, 35% aqueous tetraethylammonium hydroxide (TEAH) was added to the stock impregnation solution at a target of 117.8 micromoles OH<sup>-</sup>/ml Ag solution, to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 5

100 g of Carrier A were immersed in 300 ml of boiling 5 %w TEAH for 15 min, then immersed six times in 300 ml of boiling de-ionized water for 15 minutes each. The

- 16 -

carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then impregnated with a cesium target of 400 ppm/gram finished catalyst. In addition, 35 %w TEAH was added to the stock impregnation solution at a target of 117.8 micromoles —  
5 OH<sup>-</sup>/ml Ag, to lower the hydrogen ion activity to a "measured pH" of 13.6.

Example 6

Carrier A was subjected to carrier washing and  
10 impregnation as described in Example 1. The cesium target was 720 ppm/gram finished catalyst. In addition, TEAH was dissolved in water and added to the stock solution at a target of 117.8 micromoles OH<sup>-</sup>/ml Ag, to lower the hydrogen activity to a "measured pH" of 13.2, and NH<sub>4</sub>ReO<sub>4</sub>  
15 was dissolved in water and added to the stock solution to provide 1.5 micromoles Re/gram finished catalyst.

Example 7

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target  
20 was 450 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 7a (Comparative)

25 Carrier A was impregnated as described in Example 7; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 8

30 300 g of Carrier A were immersed in 900 ml of a boiling 0.1 M solution of ammonium acetate for 15 min, then immersed in 300 ml of de-ionized water at 25 °C for 15 minutes, followed by immersion three times in 300 ml of boiling de-ionized water for 15 minutes each. The

- 17 -

carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then impregnated as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation- solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

#### Example 9

The  $\alpha$ -alumina source material for Carrier A was washed with de-ionized water at 25 °C, then homogenized with the same ingredients used to form Carrier A before extruding, drying, and firing in a muffle furnace. The resulting carrier was designated Carrier D. Carrier D was used to prepare a catalyst in the same manner as described in Example 1. The cesium target was 510 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

#### Example 10

A catalyst was prepared from Carrier D in the same manner as outlined in Example 9; however, the carrier was not subjected to carrier washing. The cesium target was 360 ppm/gram finished catalyst.

#### Example 11

100 g of Carrier A were immersed in 300 ml of a boiling 0.1 M solution of barium acetate at 25 °C for 15 min, then immersed in 300 ml of de-ionized water at 25 °C for 15 minutes, followed by immersion three times in 300 ml of boiling de-ionized water for 15 minutes each. The carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then impregnated as described in Example 1. The cesium target was 400 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock

- 18 -

impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 12

Carrier A was subjected to carrier washing and  
5 impregnation as described in Example 1. The cesium target  
was 650 ppm/gram finished catalyst. In addition, LiOH was  
dissolved in water and added to the stock impregnation  
solution to lower the hydrogen ion activity to a  
"measured pH" of 13.2 and  $\text{NH}_4\text{ReO}_4$  was dissolved in water  
10 and added to the stock impregnation solution to provide  
1.5 micromoles Re/gram finished catalyst.

The catalysts of Examples 1-12 were used to produce  
ethylene oxide from ethylene and oxygen. 3 to 5 grams of  
crushed catalyst were loaded into a 6.35 mm inside  
15 diameter stainless steel U-shaped tube. The U tube was  
immersed in a molten metal bath (heat medium) and the ends  
were connected to a gas flow system. The weight of the  
catalyst used and the inlet gas flow rate were adjusted to  
achieve a gas hourly space velocity of 6800 ml of gas per  
20 ml of catalyst per hour. The inlet gas pressure was  
1450 kPa.

The gas mixture passed through the catalyst bed (in a  
once-through operation) during the entire test run  
(including start-up) consisted of 25% ethylene, 7.0%  
25 oxygen, 5% carbon dioxide, 63% nitrogen, and 2.0 to  
6.0 ppmv ethyl chloride.

The initial reactor (heat medium) temperature was  
180 °C. The temperature was ramped at a rate of 10 °C per  
hour from 180 °C to 225 °C, and then adjusted so as to  
30 achieve a constant ethylene oxide level of 1.5 %v in the  
outlet gas stream. Performance data at this conversion  
level are usually obtained when the catalyst has been on  
stream for a total of at least 1-2 days. Due to slight  
differences in feed gas composition, gas flow rates, and  
35 the calibration of analytical instruments used to

- 19 -

determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next.

5       The initial performance values for selectivity at 1.5% ethylene oxide were measured and are reported in —  
Table III.

TABLE III. Performance Characteristics of Catalysts Prepared From Unwashed and Washed  $\alpha$ -Alumina

Example	Carrier	Pre-Impregnation Condition	Base Addition	Impregnating Solution "measured pH"	Selectivity (%)	Temperature (°C)
1	A	water wash	none	11.2	82.7	229
1a	A	no wash	none	11.2	81.3	237
2	B	water wash	none	11.2	82.5	226
2a	B	no wash	none	11.2	82.0	232
3	C	water wash	none	11.2	82.0	229
3a	C	no wash	none	11.2	82.0	235
4	A	water wash	TEAH	13.2	82.7	226
5	A	TEAH wash + water wash	TEAH	13.6	82.7	222
6	A	water wash	TEAH	13.2	89.4	245
7	A	water wash	LiOH	13.2	82.7	226
7a	A	no wash	LiOH	13.2	82.0	227
8	A	ammonium acetate wash	LiOH	13.2	83.1	222
9	D	raw material wash + water wash	LiOH	13.2	82.7	222
10	D	raw material wash	LiOH	13.2	83.0	225
11	A	barium acetate wash	LiOH	13.2	82.7	226
12	A	water wash	LiOH	13.2	86.2	232

- 21 -

It can be seen that significant improvement in catalyst properties are seen when the sodium solubilization rate is lowered. Carriers A and B have dramatically lower sodium solubilization rates (see Table II) after being subjected to the Carrier Washing Procedure. Notice that despite the lower bulk sodium for Carrier C, it has a high sodium solubilization rate. Even further improvement is seen when the material used to make the carrier is washed before the carrier is formed, Carrier D.

The hydrogen ion activity of the deposition solution for catalysts in Examples 4-12 was lowered by the addition of a base. It can be seen that lowering the hydrogen ion activity of the deposition solution further improves the catalytic properties. It is also evident that the phenomenon of the pH effect is not restricted to a particular catalyst formulation, as best illustrated in Examples 6 and 12, where a selectivity enhancing dopant, such as rhenium, is added to the impregnating solution.

It will be apparent to one of ordinary skill in the art that many changes and modifications may be made to the invention without departing from its spirit or scope as set forth herein.

- 22 -

C L A I M S

1. A catalyst carrier having a sodium solubilization rate, as measured by the amount released by immersion in 3:1 w/w of boiling water, of no greater than 5 ppmw, basis the total weight of the carrier, per 5 minutes.
- 5 2. A process for preparing a catalyst carrier according to claim 1 wherein said sodium solubilization rate is achieved by a means effective in rendering ionizable species present on the surface of the carrier ionic and removing at least part of that species, or rendering the ionizable species insoluble, or rendering the ionizable  
10 species immobile.
3. A process according to claim 2 wherein said means is selected from washing, ion exchange, volatilizing, impurity control, precipitation, sequestration, and combinations thereof.  
15
4. A catalyst comprising a carrier according to claim 1 and one or more catalytically reactive metals and optionally one or more promoting materials deposited on said carrier.
- 20 5. A catalyst according to claim 4, characterized in that it is suitable for the vapour phase epoxidation of olefins.
6. A catalyst according to claim 5, characterized in that said carrier is an alumina-based carrier and said  
25 catalytically reactive metal is silver.
7. A process for preparing a catalyst according to claim any one of claims 4-6, characterized in that said catalytically reactive metal is deposited on said carrier by submerging the carrier in an impregnation solution the  
30 hydrogen ion activity of which is lowered.



- 23 -

8. A process for the catalytic epoxidation of an alkene with an oxygen containing gas, wherein a catalyst according to any one of claims 4-6, or a catalyst as prepared according to claim 7, is used.

5 9. A process according to claim 11, characterized in — that at least one of the nitrogen oxides is added to the oxygen containing gas.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/06725

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/50 B01J37/06 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 994 587 A (NOTERMANN THOMAS M ET AL) 19 February 1991 (1991-02-19) column 12, line 57 -column 21, line 50 claims 1-9	1-6,8,9
A	US 4 212 772 A (KOOPMANN JUERGEN ET AL) 15 July 1980 (1980-07-15) column 5, line 31 - line 42	4-6,8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 December 1999

Date of mailing of the international search report

13/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No

PCT/EP 99/06725

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4994587 A	19-02-1991	CA 1293496 A	24-12-1991
US 4212772 A	15-07-1980	DE 2622228 A	08-12-1977
		DE 2640540 A	23-03-1978
		DE 2641000 A	16-03-1978
		DE 2704197 A	31-08-1978
		BE 854801 A	18-11-1977
		FR 2351700 A	16-12-1977
		GB 1581884 A	31-12-1980
		IT 1078404 B	08-05-1985
		JP 53001191 A	07-01-1978
		NL 7705520 A	22-11-1977
		BE 867045 A	13-11-1978
		DE 2819595 A	07-12-1978
		FR 2390203 A	08-12-1978
		GB 1601635 A	04-11-1981
		IT 1206597 B	27-04-1989
		JP 1430789 C	24-03-1988
		JP 54015491 A	05-02-1979
		JP 62035813 B	04-08-1987
		NL 7805102 A	14-11-1978

**THIS PAGE BLANK (USPTO)**